

Long-Chain Vinyl Esters and Ethers. Preparation from Commercial Raw Materials

Preparation of vinyl esters on a large laboratory scale was undertaken to determine whether the production of a polymerizable grade of these monomers from acetylene and the appropriate alcohol or acid would be commercially feasible, and to estimate the selling price of vinyl stearate.

Technical vinyl stearate was obtained in 88% over-all yield (based on stearic acid) by filtration and flash distillation of the crude reaction mixture. Crystallization of the technical grade from acetone gave pure vinyl stearate in 67% over-all yield. Technical vinyl oleate was obtained in 85% yield by filtration and flash distillation of the crude reaction mixture; pure vinyl oleate, in 57% yield by fractionation of the technical grade; technical vinyl octadecyl ether and vinyl oleyl ether in 89 and 88% yields; the pure (redistilled) grades in 83 and 55% yields.

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at 210° to 220° C. was used as the heat reservoir. The average yield in the distillation step was 88.5%.

Technical vinyl stearate was further purified by crystallization from 3.2 parts of acetone at 0° C. (The products so obtained denoted in this paper as "pure" vinyl stearate.) The average yield in the crystallization step was 80.1%. An over-all average yield of 67.2% was thus obtained. The results of the series of eleven vinylations are summarized in Table I.

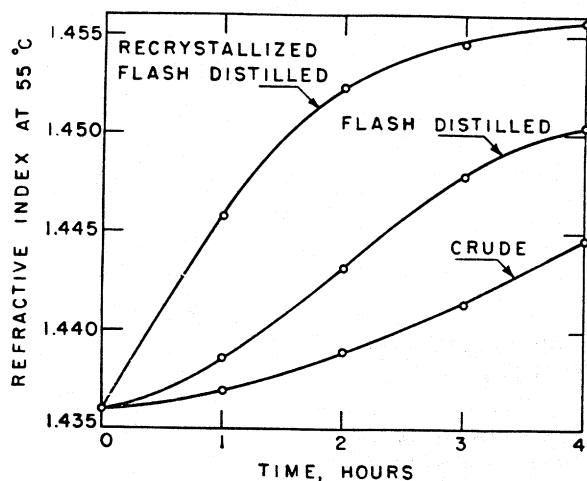


Figure 1. Rate of polymerization of vinyl stearate at 70° C. with 0.25% benzoyl peroxide

Specifications and Polymerizability. Pure vinyl stearate was a white, waxy solid, which was essentially colorless when molten. The refractive indices of the products were 1.4360 ± 0.0002 (55° C.) and the iodine number ranged from 78.1 to 81.2. Chemical analysis was frequently an inadequate measure of purity because analytically undetectable amounts of inhibitor could entirely prevent polymerization, the iodine number on repeatedly purified vinyl esters was low, and samples which had low iodine values were frequently readily polymerized. A more sensitive test for purity was based on rate of polymerization. Studies on the mass polymerization in vinyl stearate showed that the presence of inhibitors could be detected from the shape of the curve obtained by plotting percentage polymerized (as measured by the refractive index) against time. A simple, practical test and specification was developed when it was observed that samples of vinyl stearate containing 0.25% benzoyl peroxide when heated at $70^\circ \pm 2^\circ$ C. under a nitrogen atmosphere attained a minimum refractive index at 55° C. of 1.4540 and showed no inhibition period (33). [Similarly, vinyl oleate gave a copolymer with vinyl stearate (90% vinyl stearate, 10% vinyl oleate) having a minimum refractive index (n_D^{55}) of 1.4470 when heated 12 hours under nitrogen at $70^\circ \pm 2^\circ$ C. with 0.5 weight % of benzoyl peroxide.] Such samples which showed an inhibition or retardation period invariably failed to reach the specified refractive index during the test time. While it is recognized that a truer measure of absence of inhibitor could be achieved by more refined tests, such as showing the linear dependence of rate of polymerization on the square root of the initiator concentration, the pragmatic test outlined is more suitable for the purpose for which it was intended.

Mass polymerization was carried out by agitating a 6-gram sample containing 0.25% by weight of benzoyl peroxide at $70^\circ \pm 2^\circ$ C. under a nitrogen atmosphere. The polymerization was followed by change in refractive index. The curves in Figure 1 show the typical polymerization behavior of the three grades of vinyl stearate. No period of inhibition is observable for the pure grade. Further examination of the technical vinyl stearate showed that a higher catalyst concentration effected an increased

rate of polymerization (see Figure 2), and it seems probable that this material would be suitable for many uses, particularly in copolymerizations involving low ratios of vinyl stearate.

Crude and technical vinyl stearate contained significant amounts of vinyl palmitate, but this was absent in pure vinyl stearate.

Crystallized oleic acid is the basis of vinyl oleate

Pure oleic acid is not at present commercially available. The commercial product used in these investigations, Emersol 233 LL Elaine (Emery Industries, Inc.), contains 4 to 5% polyunsaturated acids, some *trans*-octadecenoic acid (elaidic acid), and some saturated C_{14} - C_{16} acids. After a number of the methods reported (3, 6, 32, 36, 38, 40) for purifying oleic acid were examined, the method adopted consisted of a single low-temperature (-55° to -50° C.) crystallization from acetone to remove the bulk of the polyunsaturated acids. The removal of the elaidic acid did not appear practical, but the vinyl esters of the lower saturated acids were removed as foreruns in the fractional distillation of the vinylation product. The single crystallization gave oleic acid containing 0.8 to 1.2% polyunsaturated acids (4, 5) in an average yield of 77%.

Vinylation of crystallized oleic acid was carried out by the procedure described above for stearic acid. The catalyst, however, was prepared from zinc acetate and crystallized oleic acid. A mixture of 2000 grams of crystallized oleic acid, 480 grams of zinc acetate, and 350 ml. of toluene was heated with agitation, water and acetic acid being removed azeotropically. After the toluene had been removed in vacuo, the residue, along with another 5800 grams of crystallized oleic acid, was charged into the 5-gallon autoclave, and vinylation was carried out to an acid number of 5 to 10.

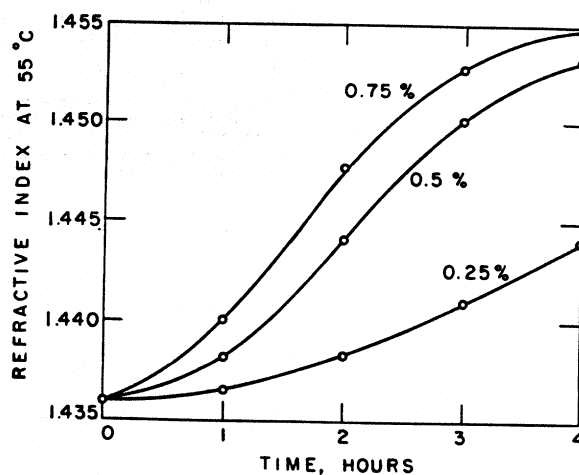


Figure 2. Effect of benzoyl peroxide concentration on rate of polymerization of technical vinyl stearate at 70° C.

The catalyst was removed by filtration to give crude vinyl oleate, which was flash-distilled at 0.5 to 1 mm. to give technical vinyl oleate in an average yield of 85%, based on the recrystallized oleic acid. As vinyl oleate polymerized much less readily than vinyl stearate, fractional distillation proved to be feasible, although pot temperatures above 210° to 220° C. resulted in products with higher acid numbers (17). Distilled (pure) vinyl oleate was obtained, in five such vinylations, in average yield of 57%. The relatively low yields were due to rather large foreruns which contained appreciable amounts of the vinyl esters of the lower saturated acids. Yields and properties of the products

Table II. Vinyl Oleate

Expt. No.	Reaction Time, Hr.	Yield, %			Properties of Pure Vinyl Oleate			
		Crude	Flash-distilled (technical grade)	Fractionated (pure grade)	B.p. range, °C.	n_D^{30}	Iodine No. (theory = 165)	Polymerization test ^a , n_D^{55}
1	9	95.0	88.4	64.1	135° (0.2 mm.) to 164° (1 mm.)	1.4538	166	1.4490
2	9	96.0	..	54.5	140° (0.5 mm.) to 167° (1.4 mm.)	1.4538	163	1.4495
3	8	99.0	..	62.0	139° (0.5 mm.) to 169° (1.6 mm.)	1.4533	163	1.4497
4	7.25	97.8	89.0	58.3	132° (0.2 mm.) to 156° (0.7 mm.)	1.4534	164	1.4490
5	4	99.0	78.6	50.0	135° (0.3 mm.) to 140° (0.4 mm.)	1.4536	160	1.4479
Av.	7.5	97.4	85.3	57.4		1.4536	163.5	1.4490

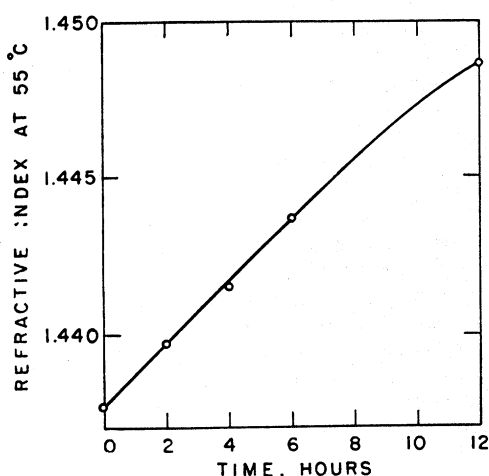
^a See Figure 3 (33).

Figure 3. Copolymerization of vinyl stearate-vinyl oleate (9 to 1) at 70° C. with 0.5% benzoyl peroxide

from five vinylations carried out by this procedure are given in Table II.

Polymerization. The pure grade of vinyl oleate was an essentially colorless liquid. Its copolymerization behavior with pure vinyl stearate is indicated by Figure 3. In this copolymerization, a solution of 4.5 grams of vinyl stearate and 0.5 gram of vinyl oleate containing 0.5% by weight of benzoyl peroxide was agitated under nitrogen at 70° ± 2° C. (33).

Vinyl ethers are prepared by vinylation of alcohols

Octadecyl Vinyl Ether. Cachalot 4-S, a U.S.P. grade of stearyl alcohol supplied by M. Michel and Co., Inc., was used without further purification for the preparation of octadecyl vinyl ether. Samples examined had octadecyl alcohol contents of 95 to 96%; the remainder was largely cetyl alcohol.

A series of ten vinylations in 5-gallon autoclaves was carried out. A mixture of 8000 grams (29.6 moles) of Cachalot 4-S, 120 grams (1.8 moles, based on 85% purity) of potassium hydroxide pellets, and 1200 ml. of toluene was heated with agitation, and water was removed azeotropically. The toluene was removed in vacuo, the residue was charged into a 5-gallon autoclave, and vinylation was carried out at 150° C. with propane-diluted acetylene at 200 pounds per square inch gage until acetylene was no longer absorbed.

The reaction product was separated from the catalyst by a rapid, short-path distillation at 1 to 2 mm. This pale yellow product, designated technical grade, was obtained in an average

yield of 89%. The vinyl ether was further purified by "topping" at 0.2 to 1 mm. through a distillation column to remove 3 to 4 weight % as a pale yellow forerun. At this point, the material distilling was essentially colorless with n_D^{30} of 1.4445. Distillation was then carried out rapidly at total take-off to give pure octadecyl vinyl ether.

The results of ten vinylations are summarized in Table III. Yields of pure ether averaged 82.5%, based on the total Cachalot 4-S charged. If the

alcohol present as the alkoxide, 1.8 moles, is considered as not being available for vinylation, the average yield was 88% of theory; similarly, the average yield of technical octadecyl vinyl ether was 95% of theory.

Pure octadecyl vinyl ether was a heavy, colorless liquid which solidified to a waxy, white solid melting at about 29° C. Boiling point ranges were not recorded, as the distillations were carried out at total take-off at different pot temperatures and rates of distillation; however, octadecyl vinyl ether boils at about 155° C.

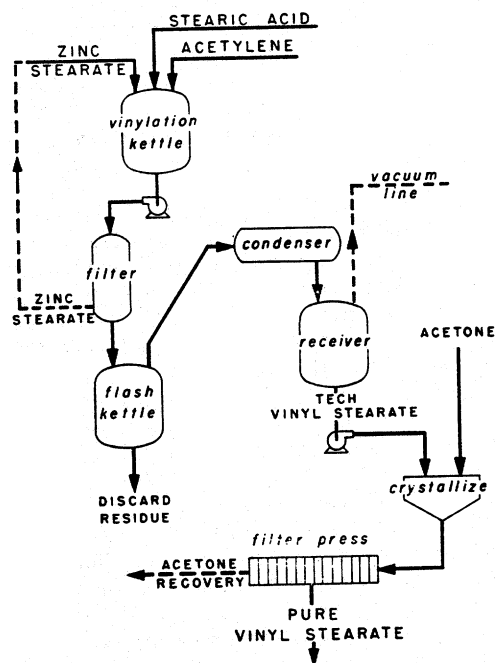


Figure 4. Flow sheet for manufacture of vinyl esters

Table III. Octadecyl Vinyl Ether

Expt. No.	Reaction Time, Hr.	Yield, %		Analyses of Pure Grade, %	
		Crude (technical grade)	Distilled (pure grade)	Residual alcohol	Vinyl ether
1	10	88.3	83.3	1.07	98.3
2	6	88.3	82.3	1.81	97.9
3	7	88.5	78.2	1.71	97.8
4	7.25	86.3	79.7	0.62	99.0
5	6.75	89.4	80.7	0.47	98.5
6	8.25	87.7	81.5	0.10	99.05
7	6.75	91.0	85.7	0.06	98.8
8	5.5	91.8	87.2	0.28	99.2
9	6.5	89.6	85.8	1.67	98.2
10	8.5	90.4	80.5	1.49	99.2
Av.	7.25	89.2	82.5	0.93	98.6

Table IV. Oleyl Vinyl Ether

Expt. No.	Reaction Time, Hr.	Yield, %		Properties of Pure Grade			
		Crude (technical grade)	Distilled (pure grade)	B.p. range, C.	n_D^{30} range	Residual alcohol, %	Vinyl ether, %
1 ^a	2.5	85.8	50.5	167-174° (2.2 mm.)	1.4530-1.4535	<0.2	99.3
2 ^b	4.5	..	54.2	161-7° (2 mm.)	1.4529-1.4534	0.25	98.0
3 ^b	3.5	..	56.2	163-7° (2 mm.)	1.4530-1.4534	0.27	100.3
4 ^b	4.7	..	57.0	163-9° (2 mm.)	1.4530-1.4536	0.27	98.3
5 ^a	2	89.5	55.7	172-5° (2.1 mm.)	1.4530-1.4535	0.3	98.6
Av.	3.5	87.6	54.7			0.26	98.9

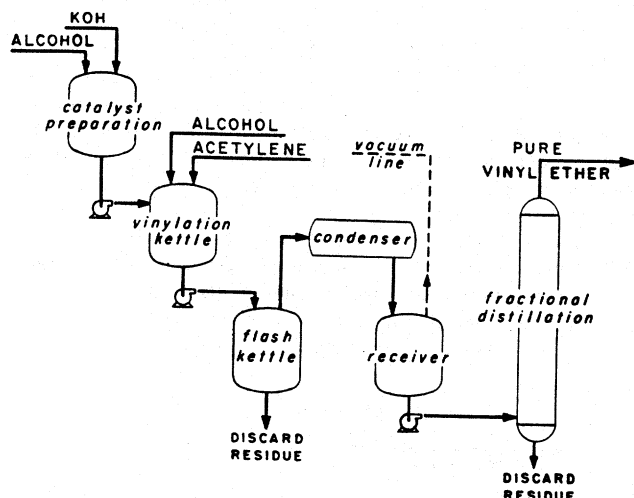
^a Cachalot 0-8 used in vinylation.^b Cachalot 0-8 fractionally distilled before vinylation.

Figure 5. Flow sheet for manufacture of vinyl ethers

at 0.5 mm. and 175° C. at 2 mm. The refractive indices of all products were n_D^{30} 1.4451 \pm 0.0002. The products from all ten of these vinylation were combined to give about 170 pounds of pure octadecyl vinyl ether with the following properties: n_D^{30} 1.4451; d_4^{30} 0.8211; freezing point, 28° C.; residual alcohol, 1%, calculated as octadecyl alcohol; vinyl ether, 98.4%, calculated as octadecyl vinyl ether (31).

POLYMERIZATION. A 150-gram sample of this combined product was stirred at 45° C. and a 10% solution of boron trifluoride etherate in dioxane added dropwise. Polymerization began after the addition of 8 drops (ca. 0.16 ml.) of catalyst solution. The exothermic reaction was moderated by cooling, and polymerization was carried out at 70° to 75° C. for 1 hour. The catalyst was destroyed by the addition of a few milliliters of ethyl alcohol, and the polymer was dissolved in chloroform and reprecipitated by pouring into acetone. The resulting polymer was a snow-white powder having the following properties: ASTM softening point (ball and ring method), 53° C.; specific viscosity (1 gram in 100 ml. of benzene), 0.26.

Oleyl Vinyl Ether. Oleyl vinyl ether was prepared by vinylation of Cachalot 0-8, a NF grade of oleyl alcohol obtained from M. Michel and Co., Inc. Cachalot 0-8 was found to contain about 81% oleyl alcohol, 14% saturated alcohols, and 5% polyunsaturated alcohols (33). It was possible to obtain essentially identical products in comparable yields by vinylation of Cachalot 0-8 followed by fractional distillation of the vinyl ether or by fractional distillation of Cachalot 0-8 followed by vinylation and distillation of the product.

The procedure for catalyst preparation and vinylation was the same as for octadecyl vinyl ether. The vinylation product from unpurified Cachalot 0-8 was separated from the catalyst by a short-path distillation to give the pale yellow technical grade of oleyl vinyl ether in 86 to 90% yields, calculated on the basis of a molecular weight of 268 for Cachalot 0-8. The pure grade

of oleyl vinyl ether was obtained as an essentially colorless liquid by fractional distillation at about 2 mm. in 51 to 56% yields. The main part of the discarded material was pale yellow foreruns which distilled at about 140° to 170° C. at 2 mm., n_D^{30} 1.4457 to 1.4527, and were largely vinyl ethers of lower saturated alcohols. Center cuts with n_D^{30} 1.4530 to 1.4535 were collected as pure oleyl vinyl ether.

In the purification of Cachalot 0-8 by fractional distillation, about 28% of the distillation charge was discarded as foreruns which were about half oleyl alcohol and half lower saturated alcohols. This purified material was vinylation in the usual way to give crude yields of 90 to 95%, based on the purified alcohol. Redistilled yields were 54 to 57%, based on the Cachalot 0-8, which were comparable to the yields obtained in the vinylation of Cachalot 0-8.

The results of five vinylation, two of unpurified Cachalot 0-8 and three of distilled Cachalot 0-8, are summarized in Table IV. All of the products were combined to give about 60 pounds of oleyl vinyl ether having the following properties: n_D^{30} 1.4532, d_4^{25} 0.8338; residual alcohol, 0.18 to 0.29%, calculated as oleyl alcohol; vinyl ether, 99.7%, calculated as oleyl vinyl ether.

POLYMERIZATION. A 150-gram sample of this combined product, which was a heavy, essentially colorless oil, was polymerized in the manner described above for octadecyl vinyl ether. Polymerization began after the addition of 9 drops (ca. 0.18 ml.) of catalyst solution. The resulting polymer was a clear, essentially colorless, viscous sirup.

Yields are high enough to be encouraging

The processes involved in the laboratory procedures described above are illustrated schematically in Figures 4 and 5. In the preparation of vinyl oleate, zinc oleate is prepared from zinc acetate and oleic acid before vinylation and the technical product is distilled for purification. Catalyst consumptions, expressed in pounds of product per pound of catalyst, and yields, based both on the acetylene and acid or alcohol, are summarized in Table V.

Table V. Catalyst Consumptions and Yields

Product	Catalyst	Catalyst Consumption, Lb. Product/Lb. Catalyst	Yields, Mole %	
			Based on acetylene	Based on acid or alcohol
Vinyl stearate	Zinc stearate	114.0	83.3	84.3
Technical grade	Zinc stearate	92.0	67.5	67.5
Vinyl oleate	Zinc acetate	319.0	88.6	65.4
Technical grade	Zinc acetate	303.0	84.1	44.2
Octadecyl vinyl ether	KOH	65.4	86.1	89.2
Technical grade	KOH	60.5	79.6	82.5
Oleyl vinyl ether	KOH	67.0	78.5	87.6
Technical grade	KOH	56.7	65.5	54.7

The yields of vinyl oleate of Table V are different from those of Table II. In Table II the yields were based on the crystallized oleic acid used in vinylation, while in Table V the loss on crystallization was taken into consideration and the yields were based on the purchased starting material, Emersol 233 LL Elaine.

(Long-Chain Vinyl Esters and Ethers)

Cost Estimate on Technical Grade Vinyl Stearate

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INDUSTRIAL interest in vinyl stearate as a comonomer has been increasing rapidly, largely because it has been demonstrated in laboratory investigations that this substance has certain outstanding characteristics for the preparation of internally plasticized copolymers with vinyl chloride (20, 23), vinyl acetate (19, 23, 24), and other monomers. One important factor which determines industrial acceptance and use of a new monomer is its cost.

This paper attempts to answer certain questions regarding the cost of production and sale of vinyl stearate. The cost estimate given is based solely on laboratory data for the preparation of vinyl stearate, described in the preceding article (page 1702). No pilot plant results are available; consequently many engineering factors have not been evaluated. Furthermore, the cost information given is for a completely new plant and not an adjunct to any existing plant.

Laboratory work has shown that the technical grade of vinyl stearate and, for some copolymerizations, the crude grade (as defined on pages 1703-4) are satisfactory monomers for use in copolymerizations. For example, copolymers of vinyl chloride containing at least up to 35% crude vinyl stearate did not differ in properties from similar copolymers prepared with pure vinyl stearate.

Production of vinyl stearate appears commercially feasible

Process. Vinyl stearate is prepared from stearic acid (95% stearic acid and 5% palmitic acid, melting point 65-67° C.) by vinylation at 165° C., with propane-diluted acetylene under a pressure of 200 pounds per square inch gage, using zinc stearate as a catalyst. This crude product is purified by flash distillation under an absolute pressure of 0.5 to 1.0 mm., giving technical vinyl stearate.

Yield of crude vinyl stearate, after vinylation, is 94% based on the theoretical yield from stearic acid. Yield of technical, after flash distillation, is 84.3% based on the theoretical yield from stearic acid.

Operations. The estimate given here is based on the production of approximately 5,000,000 pounds of technical grade vinyl stearate per year. Also given (Table V) are the basic figures for the production of 1,000,000 and 10,000,000 pounds of technical grade vinyl stearate per year obtained by ratios from the calculations for 5,000,000 pounds per year.

Production of 15.625 pounds of technical grade vinyl stearate per day or 5,000,000 pounds per year (Table III) is calculated as follows:

Raw material per charge	Pounds
Stearic acid	2850
Zinc stearate, U.S.P.	416

Average yield, based on 1.0839 theoretical yield from stearic acid, is 84.3%:

Yield per charge	Pounds
2850×1.0839	3089.12
3089.12×0.843	2604.13

Make 2100 charges per year operating 24 hours per day, 350 days per year:

$$2604.13 \text{ pounds/charge} \times 2100 = 5,468,673 \text{ pounds/year} \\ 15.625 \text{ pounds/day}$$

Return on Investment. The estimate is based on a net return of 12%, after taxes, calculated on the fixed capital investment. This estimate is composed of five parts: equipment (Table I), capital expenditures (Table II), cost sheet (Table III), operational analysis (Table IV), and summary (Table V).

Conclusions and Discussion. Monomers to be used as internal plasticizers must not only yield copolymers that have desirable properties, but they must also be available in the usually accepted price range of external plasticizers (30 to 50 cents per pound) in order to furnish a sufficient motivation for their large scale use. For specialty applications, where permanence of plasticizer is absolutely essential, this restriction does not apply.

At a production rate of 5,000,000 pounds per year it should be possible to build a plant and manufacture and sell vinyl stearate at a profit, after taxes, at a selling price of about 48 cents per pound. At an annual production rate of 10,000,000 pounds, the selling price could be about 35 cents per pound.

However, these cost estimates include not only building an entirely new plant, but also the step of washing the catalyst with acetone followed by acetone recovery. This step was employed in the laboratory study to obtain accurate yield figures, because the catalyst separated from the autoclave charge contained significant amounts of vinyl stearate adhering to it. There appears to be no reason why the unwashed catalyst cannot be

This article describes large scale laboratory preparation, in high yield, of vinyl stearate, vinyl oleate, vinyl octadecyl ether, and vinyl oleyl ether from acetylene and the appropriate commercial grade of long-chain acid or alcohol. The synthesis of these monomers of purity sufficiently high to ensure polymerizability seems commercially feasible. The monomers have potential commercial interest because their basic raw materials (acetylene and tallow) are inexpensive and readily available. In the copolymers prepared, the long chain is chemically bound in the polymer molecule, and the resulting intramolecularly modified polymers should retain their original properties indefinitely compared with changes, due to exudation, evaporation, and leaching, encountered in plasticized polymer compositions. Cost estimates based on preliminary laboratory data indicate that a plant producing 5,000,000 pounds of vinyl stearate per year should realize a profit, after taxes, from a selling price of about 43 cents per pound; at an annual production rate of 10,000,000 pounds, the selling price could be as low as 31 to 34 cents per pound. A return of 12% on the investment, after taxes, is assumed.

Table I. Equipment

		Cost			Cost
2 acetone storage tanks	1/4-inch carbon steel, 10-ft. diameter, 15 ft. 7 inches long	\$ 4,480	Condenser, shell and tube	145.6 sq. ft. cooling surface, carbon steel	1,640
Bronze centrifugal pump	Acetone to process, 60 gal./min. at 40-ft. head. Class I-D	780	Receiver	Carbon steel, 150-gal. capacity	260
Portable conveyor	RR siding inload cars, 40 ft. X 30 inch wide side rails. Class I-D	2,570	Pump, bronze centrifugal	30 gal./min. at 25-ft. head. Class I-D	410
Conveyor, reversing, storage room	58 ft. long, 36 inches wide. Class I-D	4,160	Pump, positive delivery	Stainless steel, 16 gal./min. at 50 lb./sq. inch. Class I-D	500
Pump, propane, reciprocating	125 lb./sq. inch gage. Class I-D	600	Rotary vacuum dryer	Includes dryer, condenser, receiver, and pump. 4 ft. diameter X 20 ft.	1,947
Conveyor, storage room to melting kettle	40 ft. long, 36 inches wide. Class I-D	3,370	Steam jet	Single jet, 5-inch abs. pressure	600
Kettle to melt stearic acid and zinc stearate	No. 316, stainless steel, c.s. jacket, agitator, 600 gal.	2,850	Condenser	To kill steam from single-stage steam jet	50
Pump, molten stearic acid and zinc stearate to reactors	P.D. pump, stainless steel. max. 13,500 lb./hr. at 40 lb./sq. inch	760	Acetylene generation	From calcium carbide, \$220/ton year	57,950
Reactors (4) ^a	No. 316 stainless steel agitator and jacketed, 300 lb./sq. inch gage working pressure	102,970	Feed tank, closed	Stainless steel, carbon steel jacket, 5-ft. diameter X 5 ft.	1,050
Tanks (4) for catalyst separation	Stainless steel jacketed, agitator and decant pipe, 1269 gal.	21,060	Flash tank	No. 316 stainless steel, 100 gal., jacketed, 0.5- to 1.0-mm. pressure	1,240
Centrifuge, solid ball continuous	Stainless steel, 70 gal./min. to 2000 gal., vapor-tight, 34 X 38 inches. Class I-D	13,420	Merrill system	Hot oil to jacket of flash tank, 410-428° F., electrical immersion heater	7,850
Conveyor, screw	6 inches, stainless steel, 25 ft. long, vapor-tight, sealed feed and discharge. Class I-D	4,590	Condenser, shell and tube	No. 316 stainless steel tubes, heads, and tube sheets, carbon steel shell, 42 sq. ft.	1,020
2 tanks for collecting	Stainless steel, closed, jacketed, 5-ft. diameter, 5 ft. deep, 735 gal.	1,040	Receiver	100 gal., stainless steel, 0.5- to 1.0-mm. pressure	620
Tank for collecting	Stainless steel, closed, 4 ft. 6 inches diameter, 5 ft. 6 inches deep, 654 gal.	700	Steam jets	0.5- to 1.0-mm. pressure, 4-stage in series, intercondenser and aftercooler	5,260
Pump	Stainless steel, positive delivery, 14,700 lb./hr. at 40 lb./sq. inch	760	Condenser	Kill steam from steam jets, 13.0 sq. ft., carbon steel construction	450
Still	Stainless steel with carbon steel jacket, 5 ft. diameter, 5 ft. deep, 735 gal.	1,040	Tank, wood	6-ft. diameter X 8 ft. deep, with Fulton-Sylphon control, hot water, 160-165°F.	530
			Pump, centrifugal	Circulate hot water, 50 gal./min. at 50 lb./sq. inch	470
					\$265,080

^a Twenty pounds of charge requires 5 gallons of reactor capacity.

Table II. Capital Expenditures

Land and site preparation	20 acres at \$300/acre	\$ 16,500	Power installed	116.14 kw. Class I-D. At \$175/kw. Immersion heaters, 15 kw.	21,070
Roads and park areas	Road 800 X 20 ft. Park 300 X 60 ft. Black top, \$4/sq. yd.	15,110	Transportation facilities, trucks and industrial trucks		19,900
Railroad sidings	3000 ft. at \$9/lineal ft.	27,000	Insulation	1922 sq. ft. at \$1.46/sq. ft. plus pipe insulation	4,310
Fences	1500 ft. at \$3.50/ft.	5,250	Freight on equipment	2% of equipment cost	5,300
Buildings	120 X 80 ft. Penthouse 15 X 60 ft.; \$9.28/sq. ft. building; \$12.58/sq. ft. penthouse	100,410	Office furniture and fixtures	1% of equipment cost	2,650
Boilers	214 boiler hp. at \$78/bhp.	16,660	Analytical and research laboratory		40,000
Equipment, manufacturing	Table I		Contingencies	10% of fixed capital	112,300
Erection of equipment, mfg. foundations, supports and positioning	30% of equipment cost	79,520	Engineering fees	15% of fixed capital	168,480
Instrumentation	7.5% of equipment cost	19,880	Fire protection and safety		4,890
Piping and ductwork	Mostly stainless steel and steam traced. 40% of equipment cost	106,030			
Erection, piping and ductwork	75% of piping cost	79,520			
Heating installed	2569 sq. ft. at \$2.50/sq. ft.	6,420			
Lighting installed	Vaporproof fixtures, 61 fxt. at \$95 each, 125 outlets at \$9 each	6,920			
				Total fixed capital	1,123,200
				Working capital. Inventories, raw materials, in process, finished goods, credits, wages, etc.	463,560
				Total capital	\$1,586,760

Table III. Cost Sheet

Production, 15,625 lb. of technical vinyl stearate per 24-hour day; continuous operation 350 days per year

	Cost			Cost	
	Per day	Per pound		Per day	Per pound
Prime Cost			Indirect expenses		
Material			Fixed		
Stearic acid, 17,100 lb. at \$0.14/lb.	\$2,394.00		Insurance, public liability and fire, 1%	32.09	
Zinc stearate, 137.1 lb. at \$0.38/lb. ^a	52.08		Taxes, 2%	64.18	
Acetone, 2100 lb. at \$0.085/lb.	178.50		Interest on fixed capital, 5%	160.45	
Acetylene, 1507 lb. at \$0.14/lb.	210.98		Depreciation, 10%	320.91	
Propane, 285.3 gal. at \$0.04/gal.	11.53		Total fixed indirect expense	\$ 577.63	\$0.03697
Nitrogen, 8593 cu. ft. at \$0.60/100 cu. ft.	51.64				
Total	\$2,898.73		Nonwage payments		
Total material cost	\$2,898.73	\$0.1855	Social security	\$ 4.90	
			Workmen's compensation	9.46	
Labor			Unemployment insurance	46.33	
6 operators at \$1.75/hr.; 12 helpers at \$1.25/hr./shift	\$ 612.00	\$0.0392	Vacation time	36.60	
Total prime cost	\$3,510.73	\$0.2247	Total nonwage payments	\$ 97.29	\$0.00622
Indirect materials			Utilities		
Shipping bags, 156 at \$0.21 ea.	32.76		Power. Process. \$0.0110/kw.	\$ 36.38	
Total indirect materials	\$ 32.76	\$0.00209	Steam. Process, \$0.65/1000 lb.	53.53	
			Water. Process, \$0.05/1000 gal.	25.75	
Factory overhead			Total utilities	\$ 115.66	\$0.0074
Indirect labor			Miscellaneous		
Supervision	\$ 57.00		Maintenance, repairs, and renewals		
Watchmen, yardmen	33.15		Process	\$ 192.54	
Mechanics, etc.	28.00		Gasoline	9.10	
Office help	36.67		Factory supplies	28.88	
Truck operator	46.00		Miscellaneous factory expenses	25.00	
Chemist, works	16.00		Total miscellaneous	\$ 255.52	\$0.01635
Total indirect labor	\$ 216.82	\$0.01387	Total indirect expense	\$1,046.10	\$0.0669
			Total factory overhead	\$4,806.41	\$0.3076
			Factory cost		
			Interest on working capital, 5%	66.23	
			Research and development expense, 2%	133.54	
			Administration and general expense	133.56	
			Cost to make	\$5,139.74	\$0.3289
			Selling cost, 10%	\$ 667.70	\$0.0427
			Cost to make and sell	\$5,807.44	\$0.3716
			Profit	\$ 869.58	\$0.0557
			Selling price	\$6,677.02	\$0.4273

^a Consumption of catalyst (tech. grade) 1 lb./114 lb. product.

Table IV. Operational Analysis

(Unit, pound)

Gross sales	\$2,336,958.50
Returns, allowances, discounts	46,739.17
Net annual sales	2,290,219.33
Production cost	1,682,243.50
Gross annual profit	607,975.83
Administration, research, selling expense	327,181.02
Profit before taxes	280,794.81
Taxes, income and excess profit, 52%	146,013.30
Net annual earnings	134,781.51
Earned on fixed capital, 12%	
Earned on total capital, 8.49%	
Dollar sales per dollar invested capital	\$2.08
Net profit, earned on gross sales, 5.77%	
Net profit on net sales, 5.89%	
Selling price per pound	\$0.4273
Profit per pound	\$0.0246
Turnover of total capital used	\$1.44
Turnover of working capital, 79.8 days	
Turnover of fixed property investment	\$2.04
Turnover of fixed property investment, physical, 4.87 lb./dollar	
Break-even point, 3,243,068 lb./yr.	
% of capacity, 59.3	
Shutdown point, 1,764,688 lb./yr.	
% of capacity, 32.3	
Pay-out time, years, F&B with 3% debenture bonds, 5.01	

Table V. Summary

	1,000,000 ^a	5,468,673	10,000,000 ^a
Yearly production, lb.			
24 hr. daily production, lb.	2857	15,625	28,571
Fixed capital	\$405,470.00	\$1,123,200.00	\$1,612,920.00
Working capital	\$167,340.00	\$ 463,560.00	\$ 665,670.00
Total capital	\$572,810.00	\$1,586,760.00	\$2,278,590.00
Factory cost			
Per day	\$ 1,735.11	\$ 4,806.41	\$ 6,902.00
Per pound	\$ 0.6073	\$ 0.3076	\$ 0.2416
Cost to make			
Per day	\$ 1,855.45	\$ 5,139.74	\$ 7,380.67
Per pound	\$ 0.6494	\$ 0.3289	\$ 0.2583
Cost to make and sell			
Per day	\$ 2,096.49	\$ 5,807.44	\$ 8,339.48
Per pound	\$ 0.7338	\$ 0.3716	\$ 0.2919
Selling price			
Per day	\$ 2,410.40	\$ 6,677.02	\$ 9,588.20
Per pound	\$ 0.8437	\$ 0.4273	\$ 0.3356
Annual gross sales	\$843,640.00	\$2,336,960.00	\$3,355,870.00
Net annual earnings after taxes	\$ 48,660.00	\$ 134,780.00	\$ 193,540.00

^a Calculated from 5,000,000 lb. production: ratio for 1,000,000 lb., 0.361, and for 10,000,000 lb., 1.436.

re-used, as its only "contaminant" is vinyl stearate, the product being made in the first place.

Elimination of the acetone wash step significantly lowers the costs of equipment and processing, and also cuts down on the over-all operating time. At an annual production of 5,000,000 pounds, elimination of the acetone wash reduces the selling cost of vinyl stearate to about 42 cents per pound and at 10,000,000 pounds to about 31 cents.

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Literature cited

- (1) Adelman, R. L., *J. Org. Chem.*, **14**, 1057 (1949).
- (2) Beller, H., Christ, R. E., and Wuerth, F., U. S. Patents 2,472,084, 2,472,086 (June 7, 1949); Brit. Patent 641,438 (Aug. 9, 1950).
- (3) Bertram, S. H., *Rec. trav. chim.*, **46**, 397 (1927).
- (4) Brice, B. A., and Swain, M. L., *J. Opt. Soc. Amer.*, **35**, 532 (1945).
- (5) Brice, B. A., Swain, M. L., Schaeffer, B. B., and Ault, W. C., *Oil and Soap*, **22**, 219 (1945).
- (6) Brown, J. B., and Shinowara, G. Y., *J. Am. Chem. Soc.*, **59**, 6 (1937).
- (7) Carpenter, G. B., FIAT Final Report 935, PB 52163 (1946).
- (8) *Ibid.*, 936, PB 58441 (1946).
- (9) Copenhaver, J. W., and Bigelow, M. H., "Acetylene and Carbon Monoxide Chemistry," Reinhold, New York, 1949.
- (10) Fikentscher, H., Kuko Report 106 (April 1937), PB A 76327, listed in BSIR 5, No. 10, 850 (June 1947).
- (11) Fikentscher, H., U. S. Patent 2,016,490 (Oct. 8, 1935); Ger. Patent 634,408 (Aug. 26, 1936).
- (12) Harrison, S. A., and Wheeler, D. H., *J. Am. Chem. Soc.*, **73**, 839 (1951).
- (13) Herrmann, W. O., and Haehnel, W., U. S. Patent 2,245,131 (June 10, 1941).
- (14) Kollek, L., *Ibid.*, 2,045,393 (June 23, 1936).
- (15) Nüsslein, J., and Finck, G. von, *Ibid.*, 2,168,535 (Aug. 8, 1939), 2,234,501 (March 11, 1941).
- (16) Nüsslein, J., Finck, G. von, and Stärk, H., *Ibid.*, 2,168,534 (Aug. 8, 1939).
- (17) Paloheimo, O., *Suomen Kemistilehti*, **23**, 71 (1950).
- (18) Port, W. S., Hansen, J. E., Jordan, E. F., Dietz, T. J., and Swern, D., *J. Polymer Sci.*, **7**, 207 (1951).
- (19) Port, W. S., Jordan, E. F., Hansen, J. E., and Swern, D., *Ibid.*, **9**, 493 (1952).
- (20) Port, W. S., Jordan, E. F., Jr., Palm, W. E., Witnauer, L. P., Hansen, J. E., and Swern, D., *IND. ENG. CHEM.*, **47**, 472 (1955).
- (21) Port, W. S., Jordan, E. F., Jr., Palm, W. E., Witnauer, L. P., Hansen, J. E., and Swern, D., U. S. Dept. Agr., Bur. Agr. Ind. Chem., AIC-366 (1953).
- (22) Port, W. S., Jordan, E. F., and Swern, D., U. S. Patent 2,586,860 (Feb. 26, 1952).
- (23) Port, W. S., Kincl, F. A., and Swern, D., *Offic. Dig., Federation Paint & Varnish Clubs*, **26**, 408 (1954).
- (24) Port, W. S., O'Brien, J. W., Hansen, J. E., and Swern, D., *IND. ENG. CHEM.*, **43**, 2105 (1951).
- (25) Powers, P. O., *Ibid.*, **38**, 837 (1946).
- (26) Reppe, W., U. S. Patent 1,959,927 (May 22, 1934); Ger. Patent 584,840 (Sept. 7, 1933).
- (27) Reppe, W., U. S. Patent 2,066,075 (Dec. 29, 1936); Ger. Patent 588,352 (Nov. 2, 1933).
- (28) Reppe, W., and Schlichting, O., U. S. Patent 2,104,000 (Dec. 28, 1937).
- (29) Reppe, W., Starck, W., and Voss, A., *Ibid.*, 2,118,864 (May 31, 1938); Ger. Patent 593,399 (Feb. 8, 1934).
- (30) Rosen, R., and Sparks, W. J., U. S. Patent 2,468,516 (April 26, 1949).
- (31) Siggia, S., and Edsberg, R. L., *Anal. Chem.*, **20**, 762 (1948).
- (32) Skellon, J. H., *J. Soc. Chem. Ind.*, 50T, 131 (1931).
- (33) Swern, Daniel, Eastern Utilization Research Branch, Philadelphia, Pa., private communication.
- (34) Swern, D., Billen, G. N., and Knight, H. B., *J. Am. Chem. Soc.*, **69**, 2439 (1947).
- (35) Swern, D., and Jordan, E. F., *Ibid.*, **70**, 2334 (1948).
- (36) Swern, D., and Jordan, E. F., *Org. Syntheses*, **30**, 106 (1950).
- (37) Swern, D., Knight, H. B., and Findley, T. W., *Oil and Soap*, **21**, 133 (1944).
- (38) Swern, D., Scanlan, J. T., and Roe, E. T., *Ibid.*, **23**, 128 (1946).
- (39) Toussaint, W. J., and MacDowell, L. G., U. S. Patent 2,299,862 (October 27, 1942).
- (40) Twitchell, E., *J. IND. ENG. CHEM.*, **13**, 806 (1921).
- (41) Voss, A., and Dickhauser, E., U. S. Patent 2,047,398 (July 14, 1936).
- (42) Voss, A., and Stärk, H., *Ibid.*, 2,160,375 (May 30, 1939).
- (43) Weber, K. H., and Powers, P. O., *Ibid.*, 2,518,509 (Aug. 15, 1950).
- (44) Wulff, C., and Breuers, W., *Ibid.*, 2,020,714 (Nov. 12, 1935); Ger. Patent 600,722 (Feb. 15, 1936).
- (45) Ziegler, K., ed., "Preparative Organic Chemistry," by Hecht, O., and Kroeper, H., in Field Information Agencies Technical, U. S. Dept. Commerce, PB 99207, pp. 6-24 (1948).